



Attorney Docket No.: 0020-4746P

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Yoshiyuki HIRAGA et al. Conf.: 6683
Serial No.: 09/623,756 Group: 1713
Filed: September 8, 2000 Examiner: Donald R Wilson
For: STABILIZED FLUORINE-CONTAINING POLYMER AND METHOD FOR
STABILIZING FLUORINE-CONTAINING POLYMER

RECEIVED
JAN 16 2004
TC 1700

VERIFICATION OF ENGLISH TRANSLATION

Commissioner for Patents
P.O. Box 1450
Alexander, VA 22313-1450

Dear Sir:

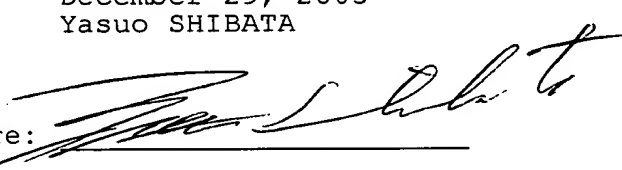
I, the below named translator, hereby declare that:

My name and post office address are as stated below;

That I am knowledgeable in the English language and in the Japanese language and that I believe that the attached English translation is an accurate translation of Japanese Patent Application No.56631/1998 filed on March 9, 1998.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: December 29, 2003
Name: Yasuo SHIBATA

Signature: 

Address: c/o AOYAMA & PARTNERS,
IMP Building, 1-3-7,
Shiromi, Chuo-ku, Osaka
540-0001 Japan

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy
of the following application as filed with this Office.

Date of Application: March 9, 1998

Application Number: Patent Application No. 056631/1998

Applicant(s): Daikin Industries Ltd.

Commissioner,
Patent Office

Document Name: Petition for Patent
Docket No.: 159765
Date of Application: March 9, 1998
Addressee: Commissioner, Patent Office
International Patent
Classification: B29B 7/00
Title of the Invention: METHOD FOR STABILIZING FLUORINE-CONTAINING POLYMER
Number of Claim(s): 10

Inventor(s):

Address: c/o Yodogawa Works of Daikin Industries Ltd.,
1-1, Nishihitotsuya, Settsu-shi, Osaka-fu
Name: Yoshiyuki HIRAGA

Address: (ditto)
Name: Satoshi KOMATSU

Address: (ditto)
Name: Tomohisa NODA

Address: (ditto)
Name: Masayuki NAMIMATSU

Applicant(s):

Identification No.: 000002853
Address: Umeda Center Building, 4-12, Nakazaki-nishi 2-chome,
Kita-ku, Osaka-shi, Osaka-fu
Name: Daikin Industries Ltd.

Patent Attorney:

Identification No.: 100062144
Name: Tamotsu Aoyama

Appointed Patent Attorney:

Identification No.: 100083356
Name: Yasuo SHIBATA

Payment of Fees:

Prepayment Book No.: 013262
Amount to be paid: 21,000

Attached document(s):

Item: Specification 1 copy
Item: Abstract 1 copy
Registration No.
of General Power: 9717866

Request for proof
transmission:

Yes

Document Name: Specification

Title of the Invention: Method for Stabilizing Fluorine-Containing Polymer

What is Claimed is:

1. A method for stabilizing a fluorine-containing polymer having terminal carboxylic acid groups or terminal groups which are hydrolyzed by heating at a temperature of at least 200°C to form carboxylic acid groups, said method comprising the steps of

adding, to the fluorine-containing polymer, 0.1 to 10% of a compound containing an alkali metal or an alkaline earth metal in terms of the number of atoms of the alkali metal or the alkaline earth metal, 0.1 to 10% of ammonia in terms of the number of ammonia molecules, or 0.1 to 10% of a compound containing ammonium groups in terms of the number of the ammonium groups, based on the total number of said terminal groups; and heating the mixture at a temperature of at least 200°C under a moist atmosphere.

2. The method according to claim 1, wherein the addition amount is from 0.2 to 5%.

3. The method according to claim 1 or 2, wherein said fluorine-containing polymer is dried and then stabilized.

4. The method according to any one of claims 1 to 3, wherein said fluorine-containing polymer is washed with water until the pH of the cleaning fluid reaches at least 4, and then stabilized in a wet state.

5. The method according to any one of claims 1 to 4, wherein the heating is carried out while said fluorine-containing polymer is melt-kneaded.

6. The method according to claim 5, wherein the melt-kneading is carried out for residence time of at least 10 minutes with a kneader which has an effective volume ratio (an effective space in a container/a space in the container) of at least 0.3, and a power factor K of less than 8,000, which is expressed by the formula: $K = Pv/\mu/n^2$ [wherein Pv is power required per unit volume (W/m^3); μ is a melt viscosity (Pa.s); and n is a unumber of revolutions per sec. (rps)].

7. The method according to claim 6, wherein said kneader is a twin-screw kneader having a self-cleaning mechanism and a piston-flow function.

8. The method according to any one of claims 1 to 7, wherein said fluorine-containing polymer is prepared by

emulsion polymerization or suspension polymerization.

9. The method according to any one of claims 1 to 8, wherein said fluorine-containing polymer is a copolymer of at least two monomers selected from the group consisting of tetrafluoroethylene, hexafluoropropylene, perfluoroalkyl vinyl ether, ethylene, vinylidene fluoride and chlorotrifluoroethylene, or a tetrafluoroethylene homopolymer, a vinylidene fluoride homopolymer or a chlorotrifluoroethylene homopolymer.

10. The method according to any one of claims 1 to 9, wherein said fluorine-containing polymer is a tetrafluoroethylene-hexafluoropropylene copolymer, a tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer or a tetrafluoroethylene-hexafluoropropylene-perfluoroalkyl vinyl ether copolymer, and has a melt viscosity of 0.1 to 100 kPa·s at 372°C.

Detailed Description of the Invention:

[0001]

Field of the Invention:

The present invention relates to a method for stabilizing a fluorine-containing polymer. In particular, the present invention relates to a method for stabilizing a

fluorine-containing polymer having terminal carboxylic acid groups and/or terminal groups which form terminal carboxylic acid groups by heating, so as to prevent the browning or grayish-browning of the polymer which is being heated, and to avoid the foaming of the polymer.

[0002]

Prior Art:

For example, in case where an emulsion copolymer of tetrafluoroethylene and hexafluoropropylene is melt-processed to obtain a final product, the final product may have bubbles or voids formed therein by a volatile material which is formed from the polymer chain ends unstable against heat and shear force.

[0003]

The kind of the unstable polymer chain end groups changes depending on the polymerization method and the types of a polymerization initiator and a chain transfer agent. For example, it is known that, when a conventional persulfate (such as ammonium persulfate, potassium persulfate or the like) is used as a polymerization initiator in an emulsion polymerization, terminal carboxylic acid groups are formed, and that such terminal carboxylic acid groups act as the source of a volatile material in the course of melt-processing of the polymer. In some cases, olefinic groups ($-\text{CF}=\text{CF}_2$), acid fluoride

groups (-COF) or the like are formed at the polymer chain ends, depending on the conditions of the melt processing. Such terminal groups may also cause bubbles or voids in a final product.

[0004]

To remove such unstable terminal groups, US-A-3,085,083 proposes the wet thermal treatment. The wet thermal treatment accelerates the treating rate by the addition of a salt or a base, and it is reported that the concentration of the salt or the base is from 100 to 600 ppm. However, the setting of such a concentration is not aimed at the unstable terminal groups.

[0005]

For example, a copolymer of tetrafluoroethylene and hexafluoropropylene prepared by emulsion polymerization may color brown or grayish brown in the course of the melt processing for obtaining a final product. Such coloration is caused by the severity of the melting conditions, the residues of the polymerization initiator, the presence of contamination, carbonization of the low molecular weight materials or the like.

The foregoing problems of the occurrence of bubbles or voids and the coloration can be solved by the fluorination disclosed in US-A-4,626,587. However, the use of fluorine for the fluorination brings about some drawbacks such as an

increase in cost and the need of a large-scale measure for preventing environmental contamination.

[0006]

Subject Matter to be Achieved by the Invention:

An object of the present invention is, therefore, to provide a method for effectively removing unstable terminal groups from a fluorine-containing polymer, thereby effectively preventing the coloration of the polymer which is caused by the unstable terminal groups, and if needed, removing also the unstable bonds on the backbone of the polymer.

[0007]

Means for Achieving the Subject Matter:

According to the present invention, the above object can be achieved by a method for stabilizing a fluorine-containing polymer having terminal carboxylic acid groups or terminal groups which are hydrolyzed by heating at a temperature of at least 200°C to form carboxylic acid groups. This method comprises the steps of adding, to a fluorine-containing polymer, 0.1 to 10% of a compound containing an alkali metal or an alkaline earth metal in terms of the number of atoms of the alkali metal or the alkaline earth metal, 0.1 to 10% of ammonia in terms of the number of ammonia molecules, or 0.1 to 10% of a compound containing ammonium groups in terms of the number of the

ammonium groups, based on the total number of the above terminal groups; and heating the mixture at a temperature of at least 200°C under a moist atmosphere.

[0008]

Modes for Carrying out the Invention:

In the method according to the present invention, a compound containing an alkali metal or an alkaline earth metal, ammonia, or a compound containing ammonium groups is added to a fluorine-containing polymer, when the polymer is heated.

Examples of the compound containing an alkali metal or an alkaline earth metal include hydroxides or salts (e.g. carbonate, sulfate, etc.) of such metals. As the compound containing ammonium groups, ammonium hydroxide or the like can be used. Preferable examples of the above compounds are potassium hydroxide, sodium hydroxide, potassium carbonate, potassium sulfate, calcium carbonate, ammonia, ammonium hydroxide, etc. Ammonia may be used in a gaseous state or in the form of aqueous ammonia.

[0009]

The addition amount of the compound containing an alkali metal or an alkaline earth metal, ammonia or the compound containing ammonium groups changes depending upon the type of a fluorine-containing polymer to be treated. The number of the metal atoms, the number of the molecules

or the number of the ammonium groups found by the above conversion is from 0.1 to 10%, preferably from 0.2 to 5% of the total number of the terminal groups to be stabilized.

When the amount of the compound containing an alkali metal or an alkaline earth metal, ammonia or the compound containing ammonium groups exceeds 10% of the total number of the terminal groups, the rate of the reaction for stabilizing the terminal groups increases, but the coloration of the polymer is not completely prevented. In addition, the polymer tends to deteriorate, and the melt viscosity decreases. On the other hand, when the amount of the compound containing an alkali metal or an alkaline earth metal, ammonia, or the compound containing ammonium groups is less than 0.1%, the molecular weight of the polymer increases when the method of the present invention is carried out in the molten state of the polymer, or the polymer is hardly stabilized when the polymer is heated at a temperature lower than the melting point of the polymer.

[0010]

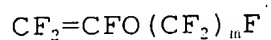
Examples of the fluorine-containing polymer which is stabilized by the method of the present invention include a copolymer of at least two monomers selected from the group consisting of tetrafluoroethylene, hexafluoropropylene, perfluoroalkyl vinyl ether, ethylene, vinylidene fluoride and chlorotrifluoroethylene, a homopolymer of

tetrafluoroethylene, a homopolymer of vinylidene fluoride, a homopolymer of chlorotrifluoroethylene, etc.

[0011]

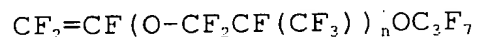
In this regard, the perfluoroalkyl vinyl ether is a vinyl ether of the formula:

[Chemical formula 1]



(wherein m is an integer of 1 to 6), or a vinyl ether of the formula:

[Chemical formula 2]



(wherein n is an integer of 1 to 4).

[0012]

When the fluorine-containing polymer to be treated is a tetrafluoroethylene-hexafluoropropylene copolymer (FEP), a copolymer comprising 72 to 96 wt. % of tetrafluoroethylene and 4 to 28 wt. % of hexafluoropropylene is preferred. When the fluorine-containing polymer is a tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA), a copolymer comprising 92 to 99 wt. % of tetrafluoroethylene and 1 to 8 wt. % of perfluoroalkyl vinyl ether is preferred. When the fluorine-containing polymer is a tetrafluoroethylene-ethylene copolymer (ETFE), a copolymer comprising 74.5 to 89.3 wt. % of tetrafluoroethylene and 10.7 to 25.5 wt. % of

ethylene is preferred.

[0013]

Each of these copolymers may comprise other monomer in such an amount that the inherent properties of the copolymer are not impaired. Examples of the other monomer include hexafluoropropylene (provided that the fluorine-containing copolymer does not comprise hexafluoropropylene), perfluoroalkyl vinyl ether (provided that the fluorine-containing copolymer does not comprise perfluoroalkyl vinyl ether), ethylene (provided that the fluorine-containing copolymer does not comprise ethylene), vinylidene fluoride (provided that the fluorine-containing copolymer does not comprise vinylidene fluoride), chlorotrifluoroethylene (provided that the fluorine-containing copolymer does not comprise chlorotrifluoroethylene), etc.

[0014]

Preferably, the fluorine-containing copolymer is prepared by emulsion polymerization or suspension polymerization. The fluorine-containing copolymer has a melt viscosity of 0.1 to 100 kPa·s at 372°C when it is a tetrafluoroethylene-hexafluoropropylene copolymer (FEP), a tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA) or a tetrafluoroethylene-hexafluoropropylene-perfluoroalkyl vinyl ether copolymer.

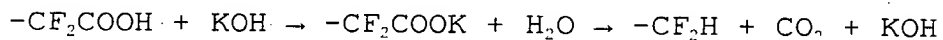
[0015]

The fluorine-containing copolymer, which is stabilized by the method of the present invention, may be either in a dry state or in a wet state. In case of the wet state, it is preferable to wash the fluorine-containing copolymer with water before the heating, until the pH of the cleaning fluid reaches 4 or more. This is because, when the polymer has a high acidity (low pH), the compound containing an alkali metal or an alkaline earth metal, the ammonia, or the compound containing ammonium groups, added to the polymer, is consumed for the neutralization reaction, and thus can not contribute to the expected stabilization of the terminal groups.

[0016]

When potassium hydroxide is used in the method of the present invention, it reacts with the terminal carboxylic acid group as follows:

[Chemical formula 3]



That is, potassium hydroxide is again formed in the course of the reaction, and again reacts with an untreated terminal carboxylic acid group to form a stable terminal group: $-\text{CF}_2\text{H}$ in sequence.

When the terminal groups are treated with ammonia or the compound containing ammonium groups, it is preferable to carry out the heating in a closed reactor, since most of

such compounds are gaseous.

[0017]

In the method of the present invention, the heating can be carried out in the melt kneading step. In this case, preferably, the residence time is at least 10 minutes, and it is preferable to use a kneader which has an effective volume ratio (the effective space in the container/the space in the container) of at least 0.3 and a power factor K of less than 8,000, provided that the power factor K is expressed by the formula: $K = P_v/\mu/n^2$ [in which P_v is power required per unit volume (W/m^3), μ is a melt viscosity (Pa.s), and n is the number of revolutions per sec. (rps)].

Particularly, in case where the fluorine-containing polymer is a copolymer, the copolymer is heated while being kneaded, and thereby, the unstable sites on the backbone, which are broken in the course of the kneading, can be converted into stable terminal groups: $-CF_2H$, via acid fluoride groups or olefinic double bonds, and carboxylic acid groups in this order.

[0018]

The kneader to be used in the method of the present invention differs from conventional twin-screw extruders, in the points of its longer residence time (at least 10 minutes, preferably 10 to 120 minutes), its structure (the effective volume ratio, etc.) and its power factor. A so-

called "surface renewal type kneader", which is preferably used in the method of the present invention, has an effective volume ratio (the effective space in the container/the space in the container) of at least 0.3, often, at least 0.5, while the effective volume ratios of the conventional twin-screw extruders are generally 0.3 or less. In this regard, the effective space in the container means the spatial volume of the container in which paddles, a shaft, etc. are equipped, while the space in the container means the spatial volume of the container in which paddles, a shaft, etc. are not equipped. Furthermore, the power factor K of the surface renewal type kneader, defined by the above formula, is 8,000 or less, often 7,000 or less, while the power factors K of the conventional twin-screw extruders are from 8,000 to 12,000. In addition, the surface renewal type kneader has a self-cleaning function and also a high piston flow function in a continuous operation.

[0019]

Typical examples of the surface renewal type kneader are HVR, SCR and NEW-SCR (all manufactured by MITSUBISHI HEAVY INDUSTRIES, LTD.); BIBOLAK (manufactured by SUMITOMO HEAVY MACHINERY AND INDUSTRIES, LTD.); Hitachi EyeGlass Paddle polymerizer and Hitachi Gate Paddle polymerizer (both manufactured by Hitachi Limited), AP-MACHINE and NEW

AP-MACHINE (both manufactured by LIST), etc. These kneaders are generally called surface renewal type kneaders.

[0020]

The treatment by the method of the present invention removes almost all the unstable terminal groups and/or the unstable bonds on the backbone, and the unstable terminal groups can be converted into stable perfluoromethyl terminal groups ($-\text{CF}_3$), difluorohydride terminal groups ($-\text{CF}_2\text{H}$), acid amide terminal groups ($-\text{CONH}_2$), methyl ester terminal groups ($-\text{COOCH}_3$) or the like.

[0021]

The amounts of the unstable terminal groups and the stable terminal groups can be quantitatively measured by IR spectroscopy, which is described in US-A-3,085,083, US-A-4,675,380 and JP-A-4-20507. The number of terminal groups can be known as the number thereof per 10^6 carbon atoms by this measuring method.

[0022]

The amount of the materials, which volatilize in the melt processing of the polymer, can be assayed by the measurement of a known volatile index: VI. Hereinafter, the method of measuring this VI value is described.

- A sample (10 g) of a polymer is charged in a heat-resistant container, and placed in a glass vessel connected to a vacuum line

- The glass vessel is evacuated to 2 mmHg or less, and inserted in a high-temperature block kept at 380°C to achieve thermal equilibrium.

- A change in pressure is recorded at intervals of 10 minutes over 60 minutes, and then a VI value is calculated according to the following formula:

$$VI = (P_{40} - P_0) \times V/10/W$$

(wherein P_0 and P_{40} are pressures (mmHg) found just before the insertion of the vessel in the high-temperature block and found after 40 minutes has passed since the insertion of the vessel in the high-temperature block, respectively; V is the volume (ml) of the vessel; and W is the mass (g) of the sample).

The volatile index is preferably 25 or less. When the volatile index exceeds 25, bubbles or voids occur which may cause troubles in the melt processing.

[0023]

Effect of the Invention:

According to the present invention, the unstable terminal groups of a fluorine-containing polymer are stabilized, and thereby, the coloration of the polymer after the melt-molding or the sintering can be prevented. In some cases, the unstable bonds on the backbone of the polymer also can be stabilized.

[0024]

Examples:Example 1

A dispersion of a FEP polymer having a melt viscosity of 2.0 kPa·s and containing 12 mol % of hexafluoropropylene, which was prepared by emulsion polymerization using ammonium persulfate (APS), was coagulated with nitric acid, and then, the polymer was dehydrated, dried, and admixed with 30 ppm of potassium hydroxide.

This polymer (1 kg) was charged in a kneader made of a corrosion-resistant material and having an effective volume ratio of 0.82 (the effective space in the container/the space in the container) (the internal volume: 1 liter), and kneaded at 50 rpm. The temperature of the kneader was set at 380°C. As soon as the kneading was started, a saturated wet air heated at 85°C was supplied at a rate of 0.1 NL/min. [0025]

The number of all the terminal carboxylic acid groups of the polymer used in this Example was 850 per 10^6 carbon atoms, and the number of potassium atoms in potassium hydroxide added to the polymer was equivalent to about 3% of the number of all the terminal carboxylic acid groups. The results are shown in Table 1. When the kneading time was 45 minutes or longer, the melt of the polymer was not colored, and the VI value was low.

[0026]

[Table 1]

Kneading time	0 min.	15 min.	30 min.	45 min.	60 min.
Total number of terminal groups -COOH, -COF, -CF=CF ₂ , etc. (per 10 ⁶ carbon atoms)	850	100	0	0	0
Melt viscosity (kPa·s)	2.0	2.1	2.0	1.9	2.1
Coloration	Brown ↔ Milky white				
VI value	120	45	15	7.5	6

[0027]

Example 2

The treatment was carried out in the same manner as in Example 1, except that 30 ppm of sodium hydroxide was used in place of potassium hydroxide. The number of sodium atoms in sodium hydroxide added to the polymer was equivalent to about 4.5% of the number of all the terminal carboxylic acid groups. The results are shown in Table 2. When the kneading time was 45 minutes or longer, the melt of the polymer was not colored, and the VI value was low, as in Example 1.

[0028]

[Table 2]

Kneading time	0 min.	15 min.	30 min.	45 min.	60 min.
Total number of terminal groups -COOH, -COF, -CF=CF ₂ , etc. (per 10 ⁶ carbon atoms)	850	135	10	0	0
Melt viscosity (kPa·s)	2.0	2.0	2.0	1.9	2.1
Coloration	Brown ↔ Milky white				
VI value	120	63	21	7.5	6

[0029]

Comparative Example 1

The treatment was carried out in the same manner as in Example 1, except that the concentration of potassium hydroxide was changed to 300 ppm. The number of potassium atoms in potassium hydroxide added to the polymer was equivalent to about 30% of the number of all the terminal carboxylic acid groups. The results are shown in Table 3. The melt viscosity of the polymer decreased, which indicated the degradation of the polymer. Even after the kneading for 60 minutes, the coloration did not disappear.

[0030]

[Table 3]

Kneading time	0 min.	15 min.	30 min.	45 min.	60 min.
Total number of terminal groups -COOH, -COF, -CF=CF ₂ , etc. (per 10 ⁶ carbon atoms)	850	55	0	0	0
Melt viscosity (kPa·s)	2.0	1.8	1.6	1.4	1.2
Coloration	Dark brown ↔ Brown				
VI value	120	41	12	6.8	6

[0031]

Comparative Example 2

The treatment was carried out in the same manner as in Example 1, except that the concentration of potassium hydroxide was changed to 0.3 ppm. The number of potassium atoms in potassium hydroxide added to the polymer was equivalent to about 0.03% of the number of all the terminal carboxylic acid groups. The results are shown in Table 4. The molecular weight increased as the kneading time became longer and longer.

[0032]

[Table 4]

Kneading time	0 min.	15 min.	30 min.	45 min.	60 min.
Total number of terminal groups -COOH, -COF, -CF=CF ₂ , etc. (per 10 ⁶ carbon atoms)	850	250	35	0	0
Melt viscosity (kPa·s)	2.0	5.0	12.5	20	32
Coloration	Brown ↔ Milky white				
VI value	120	68	35	8.5	8

[0033]

Example 3

The same polymer as that used in Example 1 (1 kg) and water (10 cc) were charged in a 3-liter autoclave. Further, an aqueous solution of ammonium hydroxide was added to the autoclave in such an amount that the number of the ammonium groups could be equivalent to 2.5% of the number of all the terminal carboxylic acid groups. Then, the mixture was heated at 230°C for 2 hours.

After the polymer was dried, the number of all the terminal carboxylic acid group was measured. As a result, the number thereof was 5 per 10⁶ carbon atoms.

[0034]

Comparative Example 3

The polymer was heated in the same manner as in Example 3, except that the aqueous solution of ammonium hydroxide was added to the autoclave in such an amount that

the number of the ammonium groups could be equivalent to 0.05% of the number of all the terminal carboxylic acid groups. After the polymer was dried, the number of all the terminal carboxylic acid group was measured. As a result, the number thereof was 450 per 10^6 carbon atoms.

Document Name: Abstract

Summary:

Purpose: To provide a method for removing, from a fluorine-containing polymer, unstable terminal groups such as terminal carboxylic acid groups, thereby effectively preventing the coloration of the polymer caused by such unstable terminal groups, and also removing unstable bonds on the backbone of the polymer.

Solution: To a fluorine-containing polymer containing terminal carboxylic acid groups or terminal groups which are hydrolyzed by heating at a temperature of at least 200°C to form carboxylic acid groups, is added 0.1 to 10% of a compound containing an alkali metal or an alkaline earth metal in terms of the number of atoms of the alkali metal or the alkaline earth metal, 0.1 to 10% of ammonia in terms of the number of ammonia molecules, or 0.1 to 10% of a compound containing ammonium groups in terms of the number of the ammonium groups, based on the total number of the above terminal groups; and the mixture is heated at a temperature of at least 200°C under a moist atmosphere.

Selected Figure: Nil